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ATOMIC REACTIONS

by

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M. POLANYI

ATOMIC REACTIONS

SECTION ONE

RECENT DEVELOPMENTS IN THE THEORY OF CHEMICAL REACTIONS

THE theory of chemical reactions shows continuous development along a number of different lines.

The classical theory founded upon the law of mass action has been undergoing constant extension right up to the present day. Within recent years, for example, it has been applied to the treatment of consecutive reactions and of chain reactions. Similarly the scope of the classical kinetic theory of gases has been steadily extended during the last fifteen years. Nevertheless, several important problems—such as the estimation of collision number in solution, and more particularly in strong electrolytes—are still waiting to be solved along the same lines.

Parallel with the development of these general principles, however, attempts have been made to reach a more intimate understanding of chemical action; for instance, endeavours have been made to elucidate the exact nature of the restriction which appears to be laid upon the formation of molecules out of free atoms by the fact that the permissible values both of the internal energy and of the rotational energy of molecules are limited by quantum laws. Again, attempts have been made to explain the internal transformations of molecules in terms of a chance accumulation of energy at critical points of the molecule due to the passing to and fro of elastic waves in its interior. Other suggestions seek to find a parallel to radioactive disintegration by conceiving chemical changes as an overtopping of potential barriers.

Yet, whilst considerations such as these have laid down with an ever greater precision the framework within which chemical change must take place, the essentially chemical features of reaction processes are left quite untouched. And these evidently cannot be explained without specific reference to chemical valency, which has been introduced into none of the considerations we have noted above.

Consequently, the new branch of chemical theory which takes valence as its starting-point, constitutes an important advance, in that it opens up for the first time a prospect of arriving at an understanding of some of the fundamentals of chemical principles.

Now various conceptions of valency are extant, which, whilst overlapping to some extent, refer in the main to different types of valence; but of these theories only that of HEITLER and LONDON has led hitherto to any deductions valid in the field of kinetics. Moreover, even within the range of validity of this theory—the exact scope of which is, as yet, a matter for discussion—it is only possible to deduce kinetic consequences in the simplest of cases, i.e. for univalent atoms the valence electrons of which occupy an S-term.

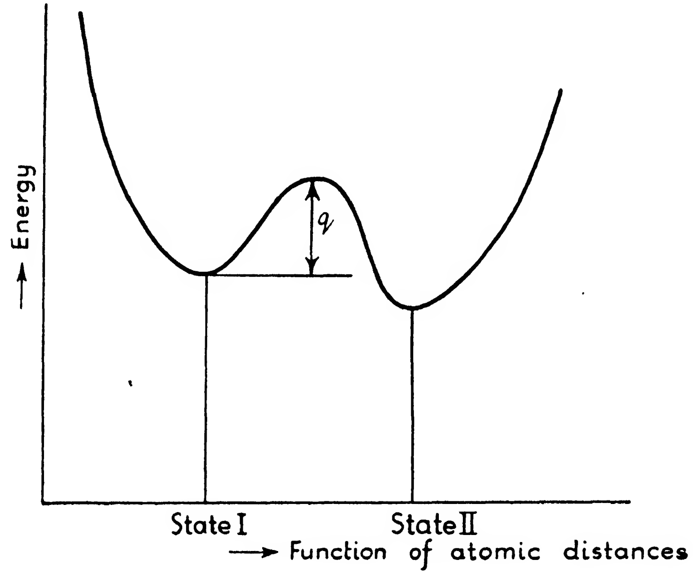

FIG. 1.—Two different chemical states characterized by minima of energy which are a function of the distances separating the atoms.

The foundation of this theory of LONDON'S[1] is an expression defining the energy of a system of atoms exclusively in terms of their mutual distances of separation. It is assumed that the different chemical states that can be formed out of a system of atoms are determined solely by differences in the atomic distances—the quantum state of the atomic system, expressed in its quantum numbers, remaining constant the while. An illustration of this conception can be given by imagining the polydimensional space of all possible atomic distances simplified to a straight line, as in Fig. 1: this figure shows that two different chemical states I and II into which a system of atoms can pass, are characterized by two minima of energy determined by the distances apart of the atoms.

If chemical change is thus to be thought of in terms of a mere variation of certain distances, we should naturally expect that these distances in the case of reacting atoms would undergo characteristic alterations during the process of chemical transformation. Fig. 2 shows by an example that this is actually the case: the diagram represents the equilibrium states of two I-atoms and two H-atoms, first as $I_2 + H_2$ and then as IH + IH. It is true that the figure gives only a rough picture of the actual state of affairs, but it suffices to bring out the essential point, namely, that there is a great difference between distances separating atoms belonging to the same molecule and those separating atoms belonging to different ones: every *inter*molecular atomic distance is much greater than any *intra*molecular distance.

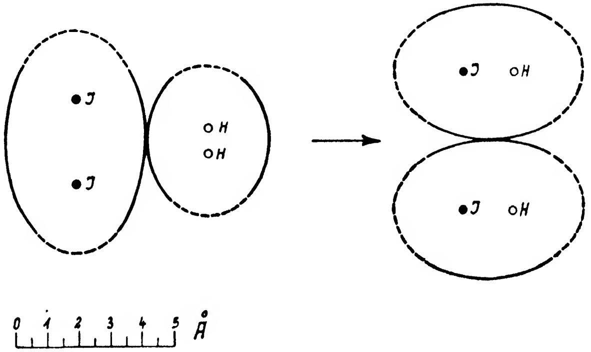

FIG. 2.—Atomic distances in the initial and final states of the reaction $I_2 + H_2 \rightarrow IH + IH$. Intramolecular distances obtained from band-spectra, and the intermolecular distances from the lattices of I_2, H_2 and HI.

From this it is evident that the essential point in bringing about a reaction is, that the system shall be forced to assume a configuration in which this essential difference between intramolecular and intermolecular distances vanishes. It is the necessity for the occurrence of this transitional state which gives rise to the energy barrier separating the two chemical states in Fig. 1. The height of this barrier is measured by the energy of activation (q) which may be determined as shown by ARRHENIUS from the temperature coefficient of the logarithm of the reaction velocity, with the aid of the formula

$$q = RT^2 \frac{d \log_e k}{dT}$$

Thus the energy of activation is seen to be the energy of formation of the state of transition in which atomic distances become approximately equalized.

A theory of chemical reaction must in the first place be able to predict correctly the magnitude of this energy.

Obviously the internal and external distances in a system of atoms could be equalized if all the existing molecular bonds were to be disrupted: the distances of completely liberated atoms could naturally assume any arbitrary magnitude and in consequence be all made equal. But it can easily be seen that this is not the way in which the chemical reactions observed under ordinary circumstances actually take place. For such a process would require an energy equal in magnitude to the dissociation energy of the participating molecules; we should thus arrive at activation energies of some 70 — 100 kg.-cal. and even more. Reactions with such large activation energies could, however, occur to a measurable extent only at high furnace temperatures.

The first and probably the most important point that a theory of chemical reactions must explain is the fact that such reactions occur at all under ordinary circumstances; that is, it must show how it is possible to level down the internal and external atomic distances with the expenditure, not of the entire energy of dissociation of the reacting compounds, but of only approximately half this quantity, i.e. 30–50 kg.-cal.

To this first fundamental point, that chemical compounds react at all under ordinary conditions, we must immediately add a second, for this reactivity is, quite clearly, severely limited. Molecules often outlast many billion collisions in which they would react if it were not for the existence of chemical inertia. The existence of our entire animate nature in the midst of an oxygen atmosphere, the existence of a great multitude of essentially unstable chemical compounds, is due to this inertia. But for this, the field of chemistry would be restricted to those substances which can exist at white heat: a million organic compounds would shrivel to a dozen or so of the simplest substances.

This stability of chemical compounds can also be expressed in quantitative terms. We may say that many of the possible modes of reaction require so great a heat of activation that they cannot occur at ordinary temperatures, which means that the compounds are usually protected by an energy barrier of at least 30 kg.-cal.

This deduction can also be reversed and at the same time amplified. All these stable compounds, in spite of their great number, comprise only a small fraction of the total range of chemical substances which are capable of existence. For beside them there is the vast number of substances which possess a free valency, and which whilst incapable of more than a transitory existence under ordinary conditions, yet are able to survive any length of time when they are in isolation. It must be concluded therefore that their reactivity is of a higher order altogether than that of saturated bodies. In the reactions of free atoms and radicals the heat of activation would thus be very low, probably less than 15 kg.-cal.

Summing up, we may say that a correct theory of chemical reactions must throw light upon the following fundamental facts:

(1) In order that chemical reactions may occur the internal and external distances of the reacting atoms must be temporarily equalized. To bring this about, it is not necessary in general to employ the entire dissociation energy of a chemical bond—an amount of less than 50 kg.-cal. being very often sufficient.

(2) At the same time it appears that for reactions between molecules with completely saturated valencies there exists a very considerable inertia, the lower limit of which corresponds to an activation heat of about 30 kg.-cal.

(3) The activation energy of the reactions of free atoms and radicals is usually below 15 kg.-cal.

Let us now examine LONDON'S above-mentioned formula which expresses the energy of a system of atoms as a function of their separations and see whether it can account for these ascertained facts of chemical reactivity.

To take the simplest case first, let us deal with the energy formula as applied to a system of three atoms. As three atoms cannot form two molecules, such an expression can, of course, only describe the reaction occurring between one free atom and a diatomic molecule; and we shall therefore expect the resulting energy of activation to be less than about 15 kg.-cal., if our above conclusions are correct. Let the three univalent atoms with S-valences we propose to examine be X, Y, Z, and the distances between them be *a*, *b*, *c* (Fig. 3, page 16). The energy w_{abc} of the system of atoms, using an approximate form of LONDON'S formula, is then given by

$$-w_{abc} = A + B + C + \sqrt{\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha} \qquad (1)$$

where A and α are functions of the distance a, only, and correspondingly B and β, C and γ functions of b and c respectively.

A, B and C are integrals of the products of the charge densities (Eigen-functions squared) of the valence electrons and are accordingly called "Coulomb terms." As the formula shows, these terms are additive, just as electric potentials would be. This part of the energy of the system is simply equal to the sum of the corresponding energies of the three atom-pairs constituting the system.

The other portion of the energy of the system is quite different in nature. The functions α, β, γ under the square root sign contain in place of the squares of the Eigen-functions of the valence electrons, the products of the Eigen-functions of the three pairs of electrons. They bear the name "exchange energies" or alternatively "resonance energies" or "resonance terms," the name being based on a mathematical analogy to the phenomenon of resonance. These "resonance terms" represent, according to HEITLER and LONDON, the valence forces. This is rendered evident by the fact that the terms of the several atom-pairs do not simply add up in the expression for the energy of the atomic system (as do the Coulomb terms) but rather assume a quadratic form which, as we shall see, brings about a saturation of resonance energies in pairs, giving them the character of valence energies.

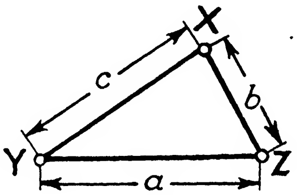

FIG. 3.

If, now, the sum total of the forces acting is to have the nature of valence, then the $\alpha\beta\gamma$ term must preponderate in the energy expression, i.e. must considerably exceed in magnitude, the ABC term. And this has actually been proved to be so by SUGIURA[2] in the case of the bond between a pair of hydrogen atoms, which can certainly be regarded as a typically homopolar valency. In this instance the Coulomb terms are found to amount only to some 5–10 per cent. of the total binding energy. It is an essential point of the LONDON theory that this result may be generalized, and we shall assume it to be so in the following argument.

The typical features of chemical changes will therefore be thrown most clearly into relief if to a first approximation we neglect the Coulomb terms and limit ourselves to an examination of the resonance part only:

$$-w'_{abc} = \sqrt{\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha} \quad . \quad . \quad . \quad (2)$$

To take a definite example we shall deal with a system of three H-atoms in which an atomic exchange reaction can take place according to the formula

$$H + H_2 \rightarrow H_2 + H$$
$$(Y + XZ \rightarrow YX + Z)$$

Such a reaction does, in fact, occur in the transformation discovered by A. FARKAS[3]

$$H + H_2^{\text{para}} \rightarrow H_2^{\text{ortho}} + H$$

so that we shall be in a position to check our special conclusions by actual measurements. But first we shall discuss the reactions of three H-atoms essentially as an example of the general behaviour of a system of three atoms.

We shall begin by considering the initial state in which the attacking H-atom (Y) is at infinity. It is characterized by the values

$$a = \infty, \quad b = b_0, \quad c = \infty$$

whence

$$-w'_{abc} = \beta_0$$

$-\beta_0$ is thus the zero point of energy.

Next, keeping $b = b_0$ let us bring up the attacking atom so near that the chemical transformation is brought about. The equalization of the internal and external atomic distances, which, as shown above, is the necessary condition for this purpose, is realized by placing the attacking

H-atom equidistant from the two atoms of the H_2-molecule, thus forming an equilateral triangle. In this case

$$a = b = c$$
$$\alpha = \beta_0 = \gamma$$
$$- w'_{abc} = 0$$

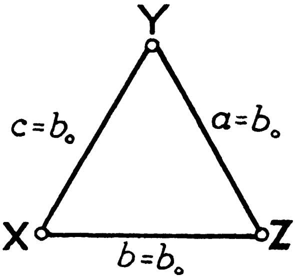

FIG. 4.—The attacking atom Y is brought to the position in which all interatomic distances are equal.

Calculating the energy from the zero point β_0, we find that to bring up this atom we have had to expend an amount of energy β_0, that is, the heat of activation required for effecting the transformation is equal (in the approximation used here) to the total energy of formation of an H_2-molecule.

Here, therefore, we have a very marked saturation of valence forces: the system of three H-atoms placed at the corners of an equilateral triangle dissociates and forms one H_2-molecule and one free H-atom thereby liberating an enormous amount of energy. The formula therefore gives a picture of the play of chemical forces which is correct qualitatively. A quantitative examination, however, reveals that it is unsatisfactory; for the height β_0 of the energy barrier is so great (about 100 kg.-cal.) as to exclude the occurrence of chemical transformations altogether under ordinary circumstances, whereas for this case we should have expected a particularly small activation energy of 15 kg.-cal. at most.

But, as already pointed out by LONDON, this only means that we have chosen a particularly unfavourable mode of attack, for it is particularly difficult to bring up the attacking atom symmetrically to the molecule XZ. The opposite extreme would be to bring up the hydrogen atom along the molecular axis; and, as LONDON has shown, the approach can be effected with the maximum ease by this path, so the transformation actually comes about in this way in practice.

In order to estimate the energy values for this path of reaction, let us imagine the attacking atom to be brought along the molecular axis of XZ up to the point where the internal and external atomic distances are equal. This configuration (Fig. 5) gives

$$c = b_0;\quad b = b_0;\quad a = 2b_0;\quad \gamma = \beta = \beta_0,\quad \alpha = f(2b_0)$$
$$-w'_{abc} = \beta_0 - \alpha = \beta_0 - f(2b_0)$$

Starting from the zero point of energy, $-\beta_0$, the formation of this configuration, according to Fig. 5, requires a total energy α equal to $f(2b_0)$, i.e. equal to the resonance energy resulting from the interaction of the two flanking atoms Y and Z. This energy corresponds to the slight residue of valence force which still remains if the H_2-molecule is extended to double its normal molecular distance; it is far smaller than the total dissociation energy β_0 that we found necessary along the equatorial path, and in actual fact is not very different from the expected figure of 15 kg.-cal.

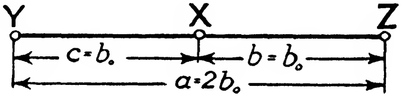

FIG. 5.—The atom Y is brought up to the molecule XZ along the axis of the latter into the position where the atomic distances are equal.

It must, however, be emphasized that this sort of calculation does not by any means give us the true magnitude of the activation energy. It merely serves as a rough illustration of the theoretical statement that the molecule is most open to attack along its molecular axis; and this statement will be employed without further proof in our following argument.

Now if we are to develop any picture of the reaction process at all, we must first of all discard the simplification which was implicit in maintaining $b = b_0$, for obviously the molecule XZ must undergo a gradual loosening as the attacking atom approaches, until finally, when $b = \infty$, the Z-atom is completely dissociated.

We have therefore to represent the energy of the three atoms, with the aid of equation (2), in terms of the parameters b and c forming a straight line, the length of which is $a = b + c$. The energy of the longitudinal transformation is thus expressed by the equation

$$-w''_{abc} = \sqrt{f(b+c)^2+f(b)^2+f(c)^2-f(b)f(c)-f(b)f(b+c)-f(c)f(b+c)} \quad (3)$$

If we take b and c to be rectangular co-ordinates, w''_{abc} can be represented, with the help of a third axis, as a three-dimensional surface.

For this system of three H-atoms chosen as an example, two ways are available for the numerical evaluation of these surfaces.

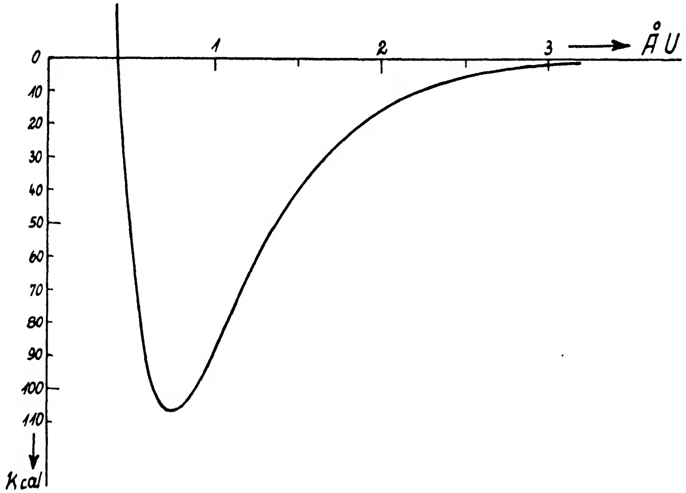

FIG. 6.—Binding energy (potential energy) of H_2 as a function of the nuclear separation, calculated from band-spectra.

The first method is to calculate the resonance energy as a function of atomic distance, as done by SUGIURA on the basis of the HEITLER–LONDON theory. This, however, is known to give only a very rough approximation.

The second method is a semi-empirical one based on a suggestion of H. EYRING, using the optically determined potential curves of the H_2-molecule. These may be considered as giving the sum of resonance energy and Coulomb energy, and as the Coulomb portion is always small compared with the resonance portion, it is permissible to a first approximation to take the optically determined potential curve as representing the resonance energy only.

Both methods of calculation have been worked through, in collaboration with H. EYRING.[4] As the final results of both methods are essentially the same, we shall limit ourselves to a description of the semi-empirical procedure.

Fig. 6 shows the potential curve as determined optically. From it, the atomic distance functions required in equation (3) are read off. The essential results of the calculation are shown in Fig. 7, where the three-dimensional w''_{abc} surface is represented as a function of b and c. As the

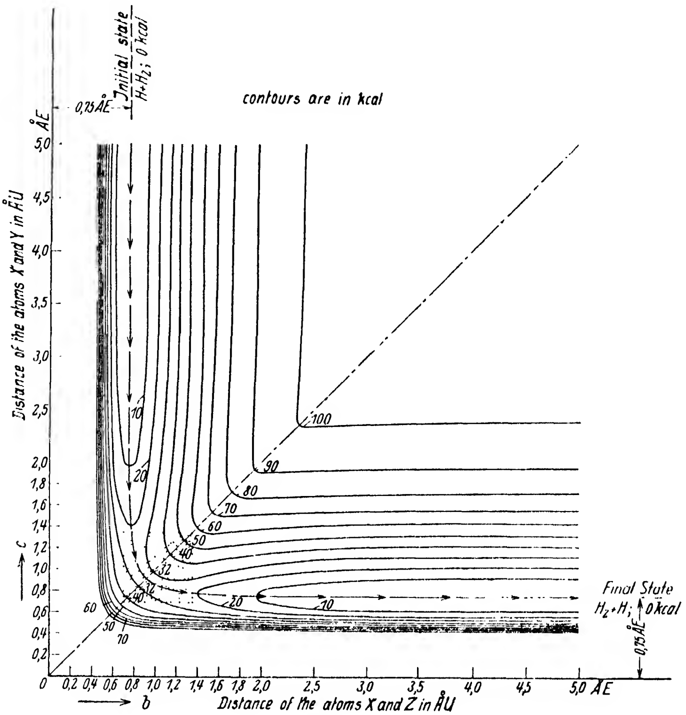

FIG. 7.—Resonance energy of three H-atoms in a straight line as a function of their distances of separation ("resonance mountain range"), calculated from the optical energy curve of H_2 neglecting the Coulomb part.

reaction is identical in both directions, b and c are naturally interchangeable and the whole figure accordingly symmetrical. The initial state is to be found at the bottom of the energy valley, where c is very great and $b = b_0 = 0{\cdot}75$ Å, the normal distance of separation of the atoms of H_2; the final state lies at the bottom of the valley for which b is very great and $c = c_0 = 0{\cdot}75$ Å.

We can visualize the chemical reaction as the movement of a point along the path shown in the diagram by a broken line. This "reaction path" starts out along the initial valley, passes up a constantly ascending slope, taking at any instant the direction of smallest potential gradient, leads to a saddle on the diagonal bisecting the two co-ordinates, and descends into the final valley, again following at any instant the direction of minimum potential gradient. At the beginning the path is parallel to the c axis: this means that the nuclear distance of the attacked molecule remains unaffected at first. The deviation of the "reaction path" away from the axis, slight at first, but constantly increasing and finally leading to a complete turn at right angles, signifies that the attacked molecule is suffering a greater and greater extension until finally it bursts asunder, with the simultaneous formation of the new molecule.

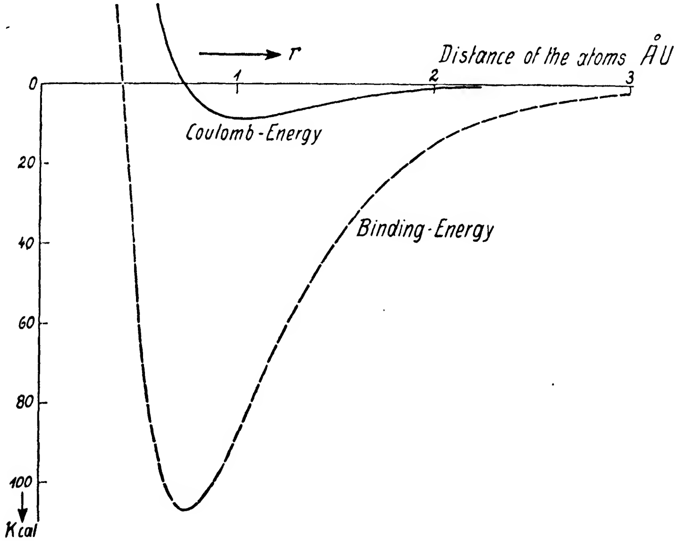

FIG. 8.—Coulomb energy curve for H_2, calculated by SUGIURA on the basis of the HEITLER–LONDON theory. For comparison the binding energy of H_2 is given as a broken curve.

The state of transition in which the atomic distances are just equalized, $b = c = 0{\cdot}9$ Å, is to be found on the diagonal at the "saddle point" of the energy surface. The height of this saddle point, measured from the initial state, is the energy which will just suffice to allow the transformation to occur—in other words, it is the heat of activation. It will be seen that the result of this first approximation, viz. 32 kg.-cal., thus turns out to be not considerably higher than we expected.

This discrepancy can, moreover, be eliminated to a large extent if we take into account the Coulomb terms that we have disregarded up till now. For this purpose we will use the Coulomb curve (Fig. 8) calculated by SUGIURA, which, although inaccurate, will give us a sufficiently good estimate of this function which, after all, is only a correction term. As the value of the heat of activation is determined solely by the saddle region, we shall limit the subsequent argument to this region. To make matters clearer, the section indicated in Fig. 7 by shading has been reproduced in Fig. 9 on an enlarged scale. The corresponding part of the Coulomb curve F(r) which is obtained by simple superposition $F(b) + F(c) + F(b + c)$ is pit-like in shape (Fig. 10, page 24); this form signifies that the Coulomb forces are not of the nature of valence but tend rather to bring together all three atoms. Were the Coulomb forces to act by themselves they would draw the atoms together into the stable state of equilibrium in which $b = c \simeq 1$ Å, i.e. a H_3-molecule with heat of formation of about 17 kg.-cal. This minimum value of the Coulomb

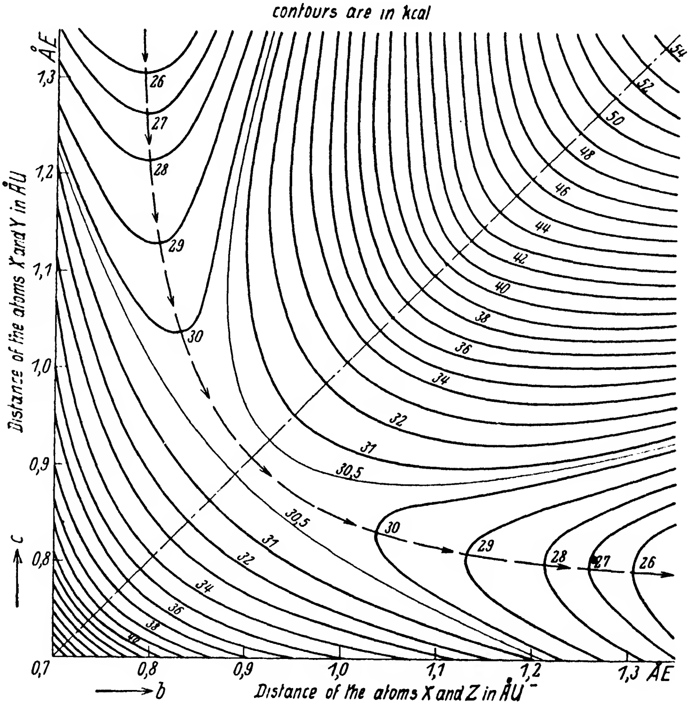

FIG. 9.—Saddle region of the "resonance range" on a larger scale.

energy is not far removed from the spot where, according to Fig. 7 and Fig. 9, the saddle of resonance energy is located. The superposition of the Coulomb basin on the latter must therefore considerably depress its height. Fig. 11, showing the results of this superposition, demonstrates further that the shape of the saddle is somewhat deformed by this operation; nevertheless it is still easy to

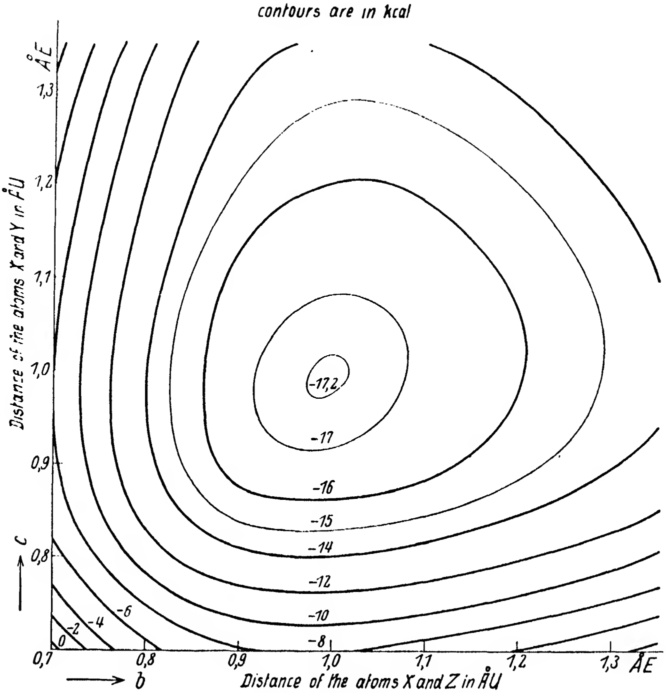

Fig. 10.—Coulomb energy of three atoms in a straight line as a function of the distances calculated from the Coulomb energy curve of H_2.

read off the maximum energy value which the reaction must traverse: it is some 20 kg.-cal.

However, this figure is still not the final value of the activation energy for it represents only the potential energy and therefore requires to be corrected with respect to zero point energy. The zero point energy in the transition state (i.e. in the saddle region) is not equal to, but considerably less than, the zero point energy in the initial state and therefore the energy needed for reaching the transition state will be less than the accompanying increase of potential energy. Thus it can be said that a portion of the zero point energy of the initial state is capable of utilization for the accomplishment of the work of activation. An estimate of this effect shows that probably the major portion of the zero point energy—which has a value of 6·5 kg.-cal.—contributes to the activation in this manner. The final result of the calculation thus falls to 15 kg.-cal., which lies in the region of the values expected.

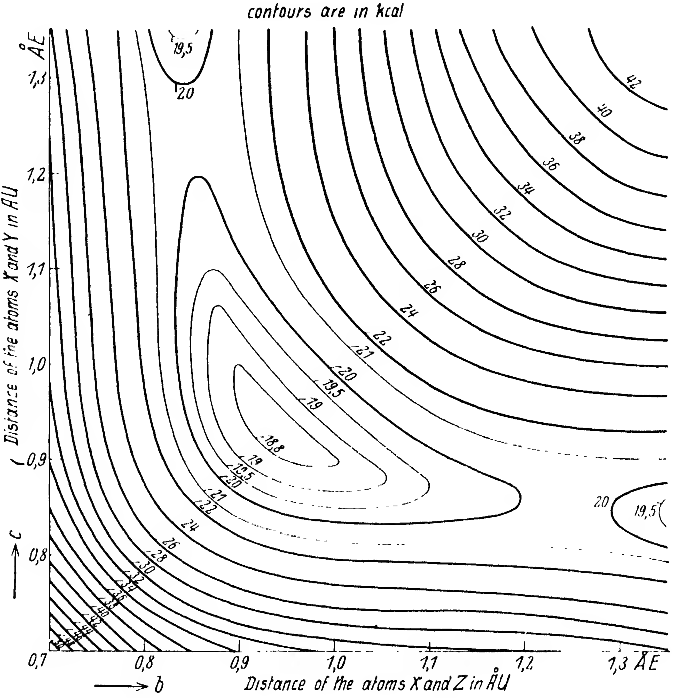

FIG. 11.—Binding energy of three H-atoms as a function of the separations obtained by superposition of the Coulomb depression on the resonance range.

In reality, of course, the activation energy of the reaction

$$H + H_2^{para} \rightarrow H_2^{ortho} + H$$

is, according to A. FARKAS, much lower, viz. 7 kg.-cal.; we shall not, however, enter here into the possible causes of this remaining discrepancy. For us it suffices that in this typical case of reaction of a free atom with a diatomic molecule the following chief features of the chemical change are correctly reproduced by the theory:

(1) The equalization of the internal and external atomic distances requires work, i.e. energy of activation.

(2) This equalization of distances, and consequently chemical reaction, can occur without employing the entire dissociation energy of a molecule.

(3) In the present particular case of a reaction between a free atom and a molecule the energy of activation constitutes such a small fraction of the dissociation energy that the reaction would immediately occur under ordinary circumstances.

Now it is easy to extend these arguments to reactions occurring between saturated molecules. The simplest of such cases is a reaction between four atoms combined into two molecules and reacting with each other according to the formula

$$XY + ZV \rightarrow XZ + YV$$

For this case LONDON has given the following energy equation

$$\begin{aligned} -w_{a_1b_1c_1a_2b_2c_2} &= A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \\ &+ \sqrt{(\alpha_1+\alpha_2)^2 + (\beta_1+\beta_2)^2 + (\gamma_1+\gamma_2)^2 \\ - (\alpha_1+\alpha_2)(\beta_1+\beta_2) - (\alpha_1+\alpha_2)(\gamma_1+\gamma_2) - (\beta_1+\beta_2)(\gamma_1+\gamma_2)} \end{aligned} \tag{4}$$

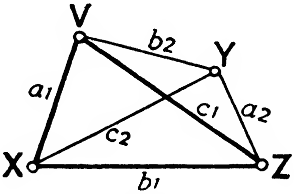

FIG. 12.

As the positions of four atoms in space are determined by six distances (Fig. 12) the formula contains six Coulomb integrals and six resonance energies corresponding to the atom-pairs in question. It goes over into the formula for three atoms if one of the atoms is removed to infinity. The effect of the addition of the fourth atom may be represented as an increase of all the exchange integrals of the system of three atoms to which it is added.

All the characteristics of chemical transformation deduced from the energy equation of the three-atom system must therefore equally be implicit in the formula applying to four atoms. Here, too, the equalization of the internal and external atomic distances will require work which appears as heat of activation. Here also this energy will in general be smaller than the dissociation energy of the reacting molecules. All this follows from the fundamental similarity between the equations for three and four atoms.

All the fundamental features of reactivity which we proposed to discuss in the first part of this paper have thus been cleared up from the theoretical point of view, with the exception of one only, viz. the greater reaction inertia obtaining in molecules as compared with free atoms or radicals. But this last point also is easy to explain, for it is obvious that two atoms combined in a molecule cannot be made to attack another molecule as favourably as can a free atom. With the free atom, an attack is possible at the spot offering the least resistance, i.e. in the direction of the molecular axis. With two atoms simultaneously this could only be done by bringing them to the two opposite ends of the molecule. To get them there, however, the bond holding them together in the molecule would first have to be stretched to such an extent that practically the entire energy of dissociation would have to be expended. This considerable extra work can only be avoided by dispensing with the access to the sensitive regions and bringing about the transformation by an approach from the side. In any case a considerably greater amount of work must be expended when two molecules react than if the reactants were free atoms.

Thus it can be seen that this empirical fact also follows naturally from the London theory.

In a quantitative respect also the application of this mechanism to molecular transformation appears to be justified. H. Eyring[5] succeeded on this basis in arriving at values for a series of reactions between binary molecules which agree with the—unfortunately very scarce—experimental material.

Perhaps the simplest case of molecular reactions is the formation of hydrogen iodide from its elements, which the author has discussed in collaboration with H. Ekstein.[6] The I_2-molecule is first of all thought of as being stretched to the extent necessary to allow the I-atoms to be brought up to the two ends of the H_2-molecule:

$$\text{(1st stage) } I_2 + H_2 \rightarrow (I + H_2 + I)$$

and then rearrangement takes place in the sense

$$\text{(2nd stage) } (I + H_2 + I) \rightarrow IH + HI$$

For the first stage it is necessary to expend very nearly the energy of dissociation of I_2, i.e. 35 kg.-cal., but for the subsequent second stage the amount required is only of the order met with in atomic reactions. Taking this latter as 0–10 kg.-cal., it is seen that the total energy required is some 35–45 kg.-cal., which agrees with the heat of activation, 40 kg.-cal., as determined by M. BODENSTEIN.

NOTE.—In a recent paper by F. PELTZER and E. WIGNER (*Z. Physikal. Chem.*, B, 15, 445 (1932)) it is established that a chemical reaction proceeds according to the LONDON mechanism if the lowest quantum state is widely separated from the others. Further, for the transformation of para-hydrogen into normal hydrogen, for which so far only the heat of activation has been calculated, it is now possible to calculate the absolute magnitudes of the velocity constants, and these have been found to agree well with experiment.

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SECTION TWO

ON ATOMIC REACTIONS WITHOUT APPRECIABLE INERTIA

THE preceding Section has shown that the theory of chemical reactions, although still very little developed, seems nevertheless already able to explain certain fundamental features of reactivity, such as the considerably higher reactivity proper to free atoms and free radicals. In addition to this the theory lays down the principles for calculating the heat of activation of certain reactions and thus gives us reason to hope that this path may soon lead to quantitative results as well. It seems therefore reasonable to endeavour to accumulate experimental material of such a kind as will provide a basis for further developments of the theory.

With this object in view we naturally turn to reactions involving free atoms, both because these are the most easily accessible to existing theory and because they would naturally, on account of their simplicity, be assumed to be the most amenable to theoretical treatment in general.

The fundamental simplicity of atomic reactions as compared with transformations of molecules having no free valencies is, in a sense, implicit in the fact that the simplest atomic reactions require only three atoms according to the formula

$$(1)\ Y + XZ \rightarrow YX + Z$$

whereas the simplest molecular reaction calls for four atoms at least

$$(2)\ YX + ZV \rightarrow YZ + XV$$

The atomic reaction accordingly breaks only *one* bond and forms only *one* bond whereas molecular reactions in general break two bonds and form two new ones.

Hence the factors governing molecular reactions are of a greater complexity. For if, in the reaction equation (1), for example, we assume an organic radical R substituted for the atom Z

$$Y + XR \rightarrow YX + R$$

and if we vary R in a homologous series by comparing the compounds XR, XR′, XR″, we may expect that the reactivity of these compounds will be determined solely by the binding forces between the atom X and the radicals R, R′, R″, and that the gradations of reactivity will accordingly be of a very simple kind. If, however, a series of homologous radicals is similarly substituted in the molecular reaction (2)

$$YX + RV \rightarrow YR + XV$$

the reactions certainly cannot depend simply on the nature of the dissolved bonds RV, R′V, R″V, but will also be influenced by the character of the newly formed bonds YR, YR′, YR″, a combination of factors the upshot of which it is difficult to foresee.

Even in the domain of ordinary molecular reactions, however, certain general rules of reactivity still hold—rules which, moreover, are fundamental in nature. It is in virtue of their existence that chemical properties can be expressed by a constitutional formula, that the few letters and dashes making up the chemical formula are able to summarize an exhaustive description of the substance. Nevertheless these rules contain inherent defects: for the inferences we are able to draw from the chemical formula of a substance as to its chemical behaviour are never more than mere probabilities, always liable to fail in any particular case.

The ultimate goal, then, of the investigation of atomic reactions, is to devise a system of clear-cut rules which will enable us to analyse the more complicated cases of ordinary chemistry; by discovering the simple rules of atomic reactions it is hoped that we may be enabled to elucidate the more complex laws of molecular transformations.

In pursuance of this aim, investigation has been made of the effect of varying the reacting substances within the limits of a given homologous series. This has naturally led to the field of organic chemistry where homologous series are the most frequent. Finally, an attempt has been made to bring the rules thus discovered into relation with the known laws of organic chemistry.

Several years before the systematic investigation of atomic reactions began, the velocity of one such reaction was determined during the course of the study of a more complex process of which it forms a part. In 1919 three authors simultaneously (HERZFELD, CHRISTIANSEN, POLANYI[1]), in quest of a theory of reaction velocity, found that the measurements of BODENSTEIN and LIND[2] concerning the formation of hydrogen bromide from gaseous elements permit of a calculation of the velocity of the reaction

$$Br + H_2 \rightarrow BrH + H$$

The result was so striking that the investigators were convinced that they were here confronted with the first example of a special class of extremely simple reactions: for it was found that in the expression for the velocity constant, viz.

$$k_1 = Se^{-\frac{Q}{RT}}$$

the factor S, which is independent of temperature, is simply equal to the number of intermolecular collisions of the reactants, so that the energy of activation, Q, is identical with the heat of reaction (which has a negative sign).

The significance attaching to this identity of the heat of activation with the negative heat of reaction is best recognized if one determines the constant k_2 with the help of the relation between the constants, k_1 and k_2, of the opposing reactions, and the equilibrium constant K

$$K = \frac{k_1}{k_2}$$

Since the equilibrium constant of a reaction which is bimolecular in both directions can, as a good approximation, be written

$$K = e^{-\frac{Q}{RT}}$$

it immediately follows that the velocity constant of the reverse reaction

$$H + HBr \rightarrow H_2 + Br$$

will have the value

$$k_2 = S$$

Here then we have a reaction which may be described as possessing *no chemical inertia*: for in the direction of the exothermic process no activation heat is required at all and the velocity constant is simply equal to the number of collisions. The energy of activation, which enters in the endothermic direction, is equal to the heat of reaction. This result led to the view, which became generally accepted, that atomic reactions have no inertia, i.e. that in the exothermic direction they have no heat of activation.

Subsequent work has shown, however, that this opinion, which, by the way, I held myself, is not correct. In the preceding Section I have already quoted an example showing this, viz. the reaction

$$H + H_2^{para} \rightarrow H_2^{ortho} + H$$

This atomic reaction has a heat of activation of 7 kg.-cal. (in both directions).

But when the task of a systematic examination of atomic reaction velocities was embarked upon about six years ago, this fact was as yet unknown and it was therefore assumed that the exothermic reaction between free atoms and molecules would occur at every collision. This assumption accordingly determined our experimental procedure. A method was worked out, in common with BEUTLER,[3] which permitted the measurement of reaction velocities far in excess of those measurable by the usual methods. A new method was necessary, for if one were to take, under ordinary circumstances—e.g. under atmospheric pressure—a gaseous mixture consisting, in equal proportions, of two substances which reacted at every collision, the reaction would be practically complete in 10^{-10} seconds, i.e. in a time too short to permit of measurement. It is scarcely practicable to retard such a reaction sufficiently by dilution, for pressures of less than 10^{-10} atmospheres (10^{-4} mm. Hg) would be necessary and in this range measurements of the rate of chemical transformation would be impossible.

One method which may be employed to measure the velocity of reactions occurring at every collision is based on the following simple principle. The two gases A and B which are to react with each other are allowed to enter into an evacuated tube at its two opposite ends (Fig. 13). The pressures of the components are chosen to be so low that the length of their mean free path shall be greater than the diameter of the tube. The resulting flow follows Knudsen's law of thermal diffusion, i.e. the two gases stream into the tube and penetrate each other after the manner of a diffusion process, without exercising any pressure on each other.

The gas A penetrating B is consumed by the reaction and its pressure gradually sinks to zero. Similarly, the pressure of B also sinks to zero as it penetrates A. In the resulting stationary state we thus have pressure curves for the components A and B as shown in Fig. 13. The reaction only occurs, of course, within the zone of mutual interpretation of A and B. The extent (U) of the reaction, proportional to the product $p_A p_B$, will thus be greatest in the centre of this zone and decrease towards both sides in a bell-shaped curve, as illustrated by Fig. 13. The essence of the method consists in inferring the reaction velocity from the ***breadth*** of this bell curve.

It is obvious in a qualitative way that some sort of connection exists between these magnitudes. For the more slowly the gases A and B react the deeper will they be able to interpenetrate without completely consuming each other. Hence, the smaller the velocity of the reaction the longer will be the zone of mutual penetration and the broader the bell-shaped curve of the reaction.

The relationship may be put into quantitative form by expressing the conditions of the stationary state in the form of a differential equation and then integrating the latter. The differential equation is based on the fact that in any cross-sectional element of volume the quantity $-dm_1$ of each substance consumed by the reaction must be exactly compensated by the quantity $+dm_2$ of the same substance accumulating there by diffusion. For a cross-sectional disc of area q and thickness dl we find that for both A and B

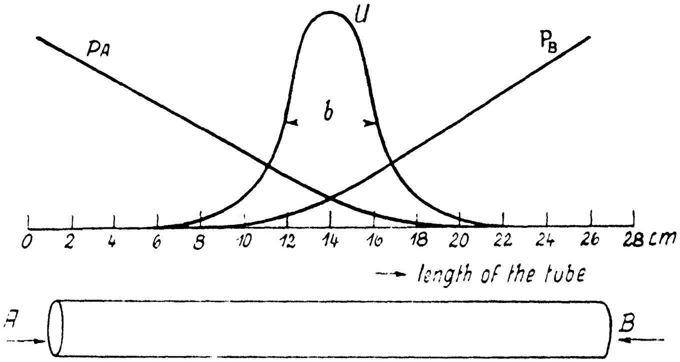


FIG. 13.—Principle of the method for measuring the velocity of reactions which take place at every or almost every collision. U = precipitate curve.

$$-dm_1 = kp_A p_B q dl$$

whilst dm_2 will be different for each component; for A

$$dm_2 = \frac{1}{K_A} \cdot \frac{d^2 p_A}{dl^2} dl$$

for B

$$dm_2 = \frac{1}{K_B} \cdot \frac{d^2 p_B}{dl^2} dl$$

where K_A and K_B are frictional constants of the flow characteristic both for the tube and for A or B. The stationary state is maintained if the equations

$$-kp_Ap_Bqdl + \frac{1}{K_A} \cdot \frac{d^2p_A}{dl^2} \cdot dl = 0$$

$$-kp_Ap_Bqdl + \frac{1}{K_B} \cdot \frac{d^2p_B}{dl^2} \cdot dl = 0$$

hold good at all points. These differential equations can be solved by a graphical method and give, for the breadth (b) of the bell-shaped curve shown in Fig. 13, the equation

$$b = 3 \cdot \sqrt[3]{\frac{1}{2kqUK_AK_B}}$$

Hence

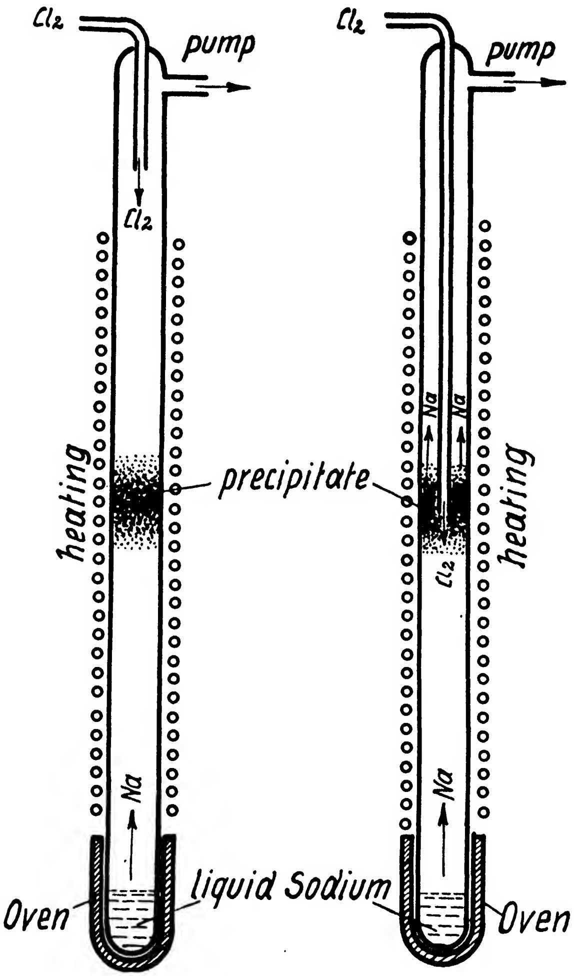
$$k = \frac{27}{b^3} \cdot \frac{1}{2qUK_AK_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Thus it is possible to calculate the velocity constant k from measurements of b, if the diffusion resistances K_A and K_B for the two gases A and B are known.

What now remains is merely the experimental problem of determining the manner in which the extent of the reaction is distributed along the tube in the stationary state so that we may be able to measure the breadth b of the distribution curve. This is comparatively easy if the gases A and B form a solid precipitate adhering to the wall of the tube. One has then simply to allow the reaction to proceed for a definite length of time, taking care the conditions remain constant, and then to measure the distribution of the precipitate along the wall of the tube.

This method has been applicable in all the cases that have been investigated hitherto; for these have involved the interaction of alkali metal vapours—particularly sodium—with halogens and volatile halogen compounds, which result in the formation of the salts NaCl, NaBr, KCl, etc.; and these, being but slightly volatile, are readily retained by the walls.

As a first example of these experiments we may take the reaction of Na vapour with Cl_2 (Fig. 14 (*a*)). Na vapour and Cl_2, both at a pressure of about 0·01 mm., are allowed to enter the two opposite ends of an evacuated tube about 1 m. long and 3 cm. wide, heated to about 300° C. The gases form a reaction zone somewhere about the middle of the tube. The reaction is observable by a gradually increasing clouding of the tube wall resulting from a desposit of NaCl. Another phenomenon produced by the reaction is a strong luminescence which we shall discuss later. At the end of about ten minutes the flow of the reacting gases


Cl₂
pump
Cl₂
heating
precipitate
Na
Oven
liquid Sodium
Cl₂
pump
Na
Na
Cl₂
heating
Na
Oven

(a) SIMPLE TUBE (b) JET ARRANGEMENT

FIG. 14.—Diagram of the experimental arrangement for the highly diluted flames. (Example Na + Cl_2.)

is stopped and the distribution of the deposit examined. This is best done optically, by measuring the opacity caused by the deposit. An example of a distribution curve determined by this method is shown in Fig. 15. The breadth *b* here amounts to 4·4 cm. Using the values of K_A and K_B determined by special streaming experiments, this gives, according to equation (5), a value for the velocity constant (in mol./c.cm.) of

$$k = 4 \cdot 10^{14}$$

On the other hand, if every collision led to reaction, the value of the velocity constant (calculated on the basis of the usual diameters of Na and Cl_2) would be

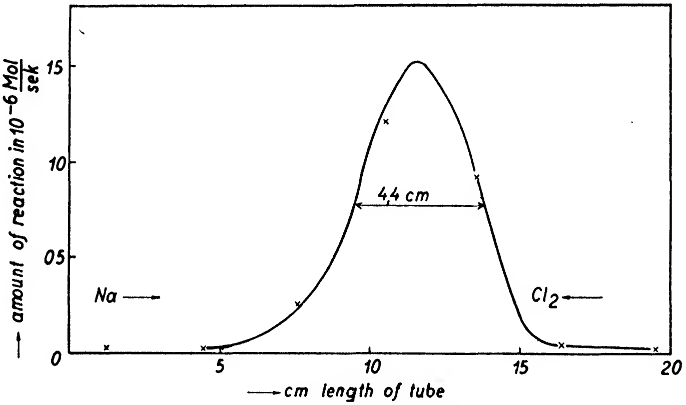


FIG. 15.—Example of an experimental precipitate curve.

$$k' = 0 \cdot 6 \times 10^{14}$$

It thus appears that, not only does every collision lead to reaction, as we expected, but further that the collision diameter is some seven times larger than the usual value deduced from gas theory.

This, however, does not give us a perfectly definite picture. In order to arrive at this we must first find out the chemical mechanism according to which Na-vapours react with Cl_2. The reaction cannot possibly take place according to the usual scheme

$$2Na + Cl_2 \rightarrow 2NaCl$$

for the collisions of 2Na-atoms with a Cl_2-molecule occur too seldom by several powers of ten to give rise to the order of magnitude found by experiment. The transformation must therefore take place in steps, of which the first is either

$$Na + Cl_2 \rightarrow NaCl_2$$

or else

$$Na + Cl_2 \rightarrow NaCl + Cl$$

A further possibility which suggests itself is that the transformation does not take place in the gas phase at all, as we have assumed hitherto, but rather as a wall reaction, and this would of course render nugatory all the previous significance which we have endeavoured to attach to the experimental results.

This last possibility is, however, eliminated by an examination of the *chemiluminescence* we mentioned before as being excited by the reaction. The luminescence is due to a chemical excitation of the D-line, which has already been examined under different experimental conditions by Haber and Zisch,[4] and as the authors have already recognized, owes its origin to the fact that molecules produced by the reaction and carrying a large amount of the energy liberated by the reaction, collide with Na-atoms and excite the latter. Our reactions, occurring as they do in a high vacuum, develop this luminescence with a much higher intensity than has been obtained heretofore, because no foreign gas is present to carry off the energy of reaction in the form of heat. How strong this light can be is shown by the photograph (Fig. 16, page 38), taken with an exposure of less than a second. It is this peculiar property of producing light which has led to the name "highly dilute flames."

The experiment photographed in Fig. 16 was arranged in a somewhat different manner from those previously discussed. In order to render the luminescence especially intense, the halogen—i.e. the chlorine in this case—must be introduced into an excess of sodium as indicated by Fig. 14 (*b*). This is done by passing the chlorine through a narrow tube, centrally inserted, whence it escapes through the jet into the greater flow of sodium vapour passing through the wider tube. The main reason why the resulting luminescence is so intense will be discussed later; it is only incompletely explained by the fact that there is a smaller number of energy-rich molecules which reach the wall without colliding with sodium atoms and are thus lost for the production of light.

The intense light yielded by this so-called "jet arrangement" makes it particularly suitable for the study of the chemiluminescence of highly dilute flames; and investigation of such jet flames has accordingly supplied the chief data for explaining the luminescence phenomenon and the chemical reactions underlying it.

The first point to be noted about the luminescence of the jet flame of Na-vapour and chlorine is the peculiar fact that the light is distributed over a much greater length than the precipitate. An example of this, obtained by measuring the distribution of light as well as that of the precipitate, is shown in Fig. 17. In the left-hand part of the figure the calculated distribution of the Na-vapour pressure is also shown. We see that this pressure is fairly constant along the main reaction zone and that in any case the reason for the difference in distribution between light and deposit cannot be sought in the non-uniformity of the Na-vapour pressure.

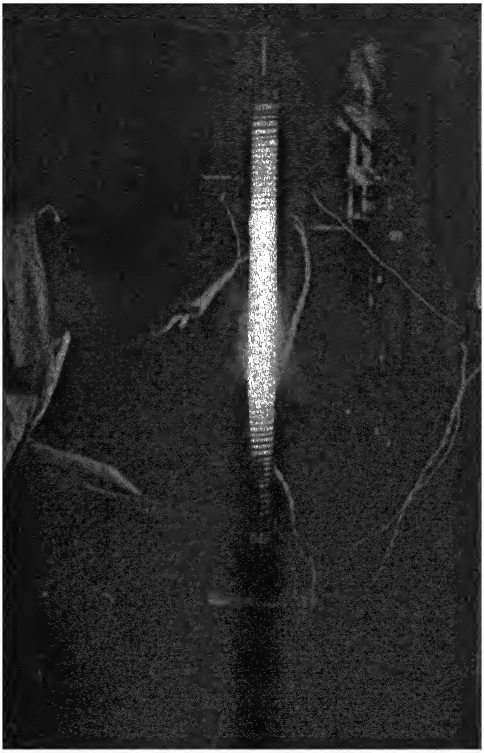


FIG. 16.

The significance of these distribution curves lies in the proof they furnish that the reaction really takes place in two stages.

As the Cl_2-molecules enter the Na-vapour they first react with great rapidity without producing light. This stage is followed by a second which gives rise to the light, and is known to be going at a slower rate because of the greater extension of the accompanying luminescence.

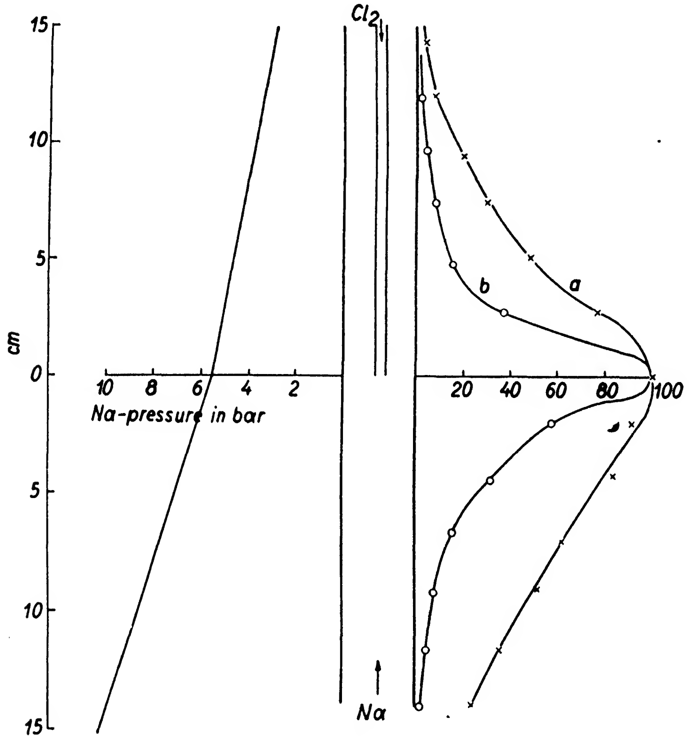


FIG. 17.

Pressure of the Na-vapour (calculated).

Distribution of (*a*) light and (*b*) amount of reaction in the jet flame.

The precipitates formed in the two stages are superimposed as shown in Fig. 18 (page 40) and form a bell-shaped curve, the breadth of which is very nearly identical with the breadth of the non-luminescent primary reaction. A further analysis then reveals the nature of the two stages of the reaction.

The primary reaction takes place entirely in the gas phase according to the scheme

$$Na + Cl_2 \rightarrow NaCl + Cl$$

As the heat of this reaction is only 35 kg.-cal., it supplies only some two-thirds of the energy required for the excitation of the sodium atom, which is 48·3 kg.-cal per g.-atom. Hence this first stage of the reaction cannot produce the light, a conclusion quite in accordance with our experimental results.

Now the chlorine atoms liberated by the primary process react in the secondary reaction with the excess sodium vapour and in so doing produce the light. It is interesting to note the details of this process.

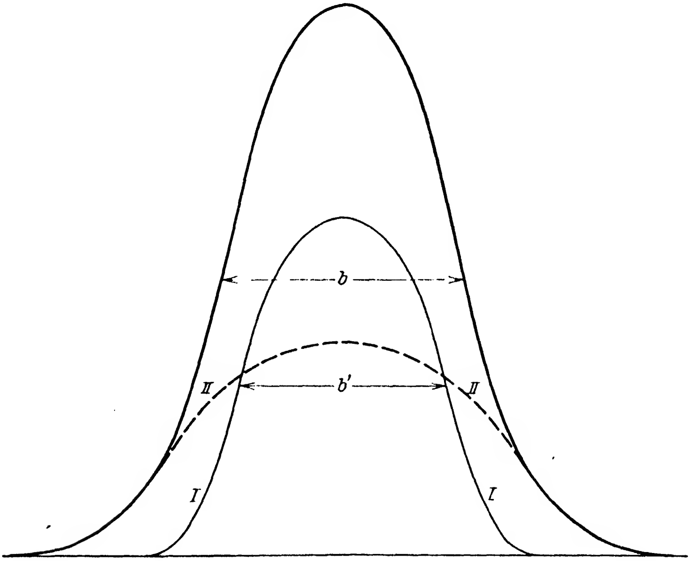


FIG. 18.—Separation of the precipitate curve into (I) primary and (II) secondary reaction (schematically).

b = breadth of the experimental curve,
b′ = breadth of the primary reaction curve.

It appears that the Cl-atoms do not unite with the Na-atoms in the gas phase, just as might be expected from the three-body collision theory. Accordingly the Cl-atoms can react in the gas phase only with the portion of the sodium vapour which consists of molecules and amounts to only a few thousandths of the whole. This stage is represented by

$$(2a)\quad Cl + Na_2 \rightarrow NaCl + Na$$

This reaction yields about 70 kg.-cal. and is therefore able to excite the D-line. For the greater part, however, the Cl-atoms do not react in the gas phase at all, but unite with the Na-atoms on the wall of the tube:

$$(2b)\ \mathrm{Cl} + \mathrm{Na} \rightarrow \mathrm{NaCl}$$

The most important confirmatory evidence for the primary reaction ($Na + Cl_2 \rightarrow NaCl + Cl$) is the fact that the presence of free Cl-atoms formed by the reaction can be proved by chemical tests: if H_2 or CH_4 be admitted to the system, HCl or CH_3Cl respectively, is formed.

The proofs of this mechanism cannot be given in full, but the more important points should be mentioned.

A certain measure of support for the assumption that the secondary gas reaction follows the mechanism

$$\mathrm{Cl} + \mathrm{Na_2} \rightarrow \mathrm{NaCl} + \mathrm{Na}$$

is given by the lower speed of the secondary reaction, manifested in the greater breadth of the light zone. We shall see that other reactions in whose mechanism sodium molecules play no part do not give rise to broader luminescence zones of this kind. A real proof of the assumed secondary reaction is however supplied by the fact that the intensity of the light can be considerably diminished and, indeed, almost completely extinguished, by raising the reaction zone to a higher temperature by heating from the outside. This is difficult to explain in any way other than by supposing that the rise in temperature dissociates the Na_2-molecules and thus slows down the light-producing reaction

$$\mathrm{Cl} + \mathrm{Na_2} \rightarrow \mathrm{NaCl} + \mathrm{Na}$$

This relationship can also be established quantitatively: the decrease of light resulting from the overheating of the reaction zone follows the typical exponential form of the dissociation curve, a straight line being obtained when log I is plotted against $1/T$ (Fig. 19, page 42). Furthermore, the slope of this straight line is found actually to correspond to the heat of dissociation of

$$\mathrm{Na_2} \leftrightarrows 2\mathrm{Na}$$

For the value we thus obtained for the heat of dissociation was $18{\cdot}5 \pm 0{\cdot}5$ kg.-cal., which stands in excellent agreement with that of LADENBURG and THIELE,[5] who arrive at a value of 18 kg.-cal., from the band-spectrum of Na_2 and the vapour pressure of sodium.

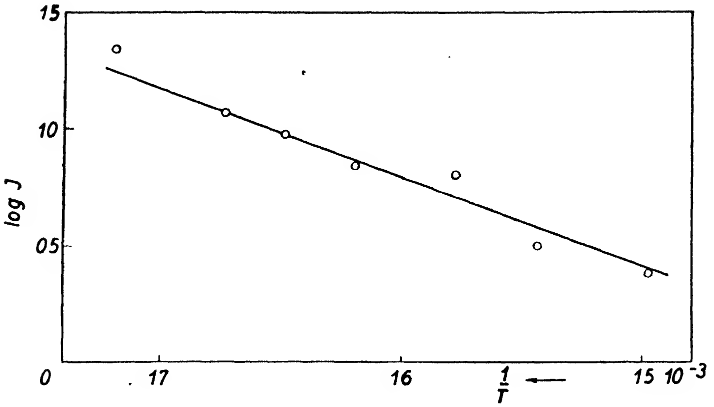


FIG. 19.—Weakening of the luminescence of the (Na + Cl_2)-flame by overheating of the reaction zone. I = intensity of light.

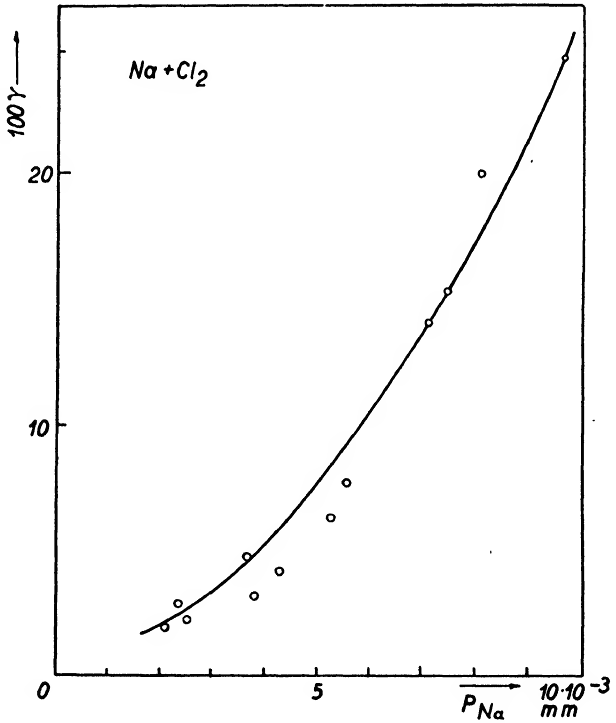


FIG. 20.—Dependence of the light yield γ on the partial pressure of the Na-vapour for Na + Cl_2.

$$\gamma = \frac{\text{number of light quanta emitted}}{\text{number of chlorine molecules reacting}}$$

A third fact in support of the light-producing role of the Na_2-molecules is supplied by the quantitative determination of the increase of the light yield with increasing sodium pressure. As Fig. 20 shows, the light yield, from about 1 to about 20 per cent., increases with the sodium pressure more rapidly than would correspond to a linear relation. This behaviour, which is very difficult to interpret in any alternative way, is easy to explain on our hypothesis, for the concentration of the Na_2-molecules, and with it the extent of the secondary light-producing reaction, would, of course, be approximately proportional to the square of the pressure.

The arguments here brought forward are effectively supported by measurements of the analogous highly dilute flames of Na-vapour with Br_2 and I_2 instead of Cl_2. The three phenomena typical of the light-producing effect of Na_2-molecules (broadening of the luminescence curve, extinction by heating, upward concavity of the light yield curve) are found here also. Once more the superheating experiments give, for the heat of dissociation of Na_2, a value of about 18 kg.-cal.

On the basis of this reaction mechanism we can find, by measurements on the Cl_2-, Br_2- and I_2-flames, the velocity constants of the primary gas reactions:

$$Na + Cl_2 \rightarrow NaCl + Cl$$

$$Na + Br_2 \rightarrow NaBr + Br$$

$$Na + I_2 \rightarrow NaI + I$$

and of the corresponding secondary gas reactions

$$Cl + Na_2 \rightarrow NaCl + Na$$

$$Br + Na_2 \rightarrow NaBr + Na$$

$$I + Na_2 \rightarrow NaI + Na$$

and finally of the secondary wall reactions

$$Na + Cl \rightarrow NaCl$$

$$Na + Br \rightarrow NaBr$$

$$Na + I \rightarrow NaI$$

These results are shown in Table I (see page 44).

We see that all six gas reactions take place at least as rapidly, and often at a noticeably greater speed, than that calculated on the supposition that every collision is effective. The velocity is greatest in the case of the reaction

$$Na + I_2 \rightarrow NaI + I$$

markedly decreasing in the homologous series from I_2 to Cl_2. Preliminary experiments with F_2 have led to the conclusion that this lightest member of the series gives a further very considerable decrease in the rate of reaction.

TABLE I

Halogen			Velocity Constant for the Reaction:			
	$Na + Hl_2 \rightarrow NaHl + Hl$		$Na_2 + Hl \rightarrow NaHl + Na$		$Na + Hl \rightarrow NaHl$ (wall)	
	Experimental $k \cdot 10^{-14}$	Theoretical for Reaction at every Collision $k' \cdot 10^{-14}$	Experimental $k \cdot 10^{-14}$	Theoretical for Reaction at every Collision $k' \cdot 10^{-14}$	Experimental $k \cdot 10^{-14}$	Theoretical for Reaction at every Collision $k' \cdot 10^{-14}$
Cl	4·1	0·6	1·5	0·56	0·13	1·0
Br	—	—	1·5	0·46	0·13	0·77
I	6·1	0·5	0·26	0·41	0·02	0·52

As far as they could be examined, the reactions of K-vapour with the halogens showed the same behaviour as the analogous reactions of Na-vapour. The reduction of light intensity by heating the flame zone is also found once again. The only difference is that the degree of diminution is lower than in the case of sodium flames, in accordance with the smaller heat dissociation of K_2, viz. 14 kg.-cal.

A further group of atomic reactions whose velocity and reaction mechanism may be determined by the investigation of highly dilute flames is furnished by the reactions of inorganic halogen compounds with sodium vapour. Of the reactions belonging to this group those of $HgCl_2$ and $HgBr_2$ with Na- and K-vapour, and of Na-vapour with $CdCl_2$, $CdBr_2$ and CdI_2, as well as with the hydrogen halides HCl, HBr, HI, have been examined in detail up to the present.

The salts of the bivalent metals, $HgCl_2$, $HgBr_2$, and also $CdCl_2$,

$CdBr_2$ and CdI_2, all follow an identical mechanism which we shall describe in the instance of $HgCl_2$. The reaction takes place in two steps:

$$\text{Primary reaction:} \quad Na + HgCl_2 \rightarrow NaCl + HgCl$$
$$\text{Secondary reaction:} \quad Na + HgCl \rightarrow NaCl + Hg$$

the heats of reaction of the two reactions being 27·2 and 56·0 kg.-cal. respectively.

We see here also that only one of the two stages, i.e. the secondary one, has a heat of reaction great enough for the excitation of light, and may therefore be considered as the sole source of the luminescence phenomenon.

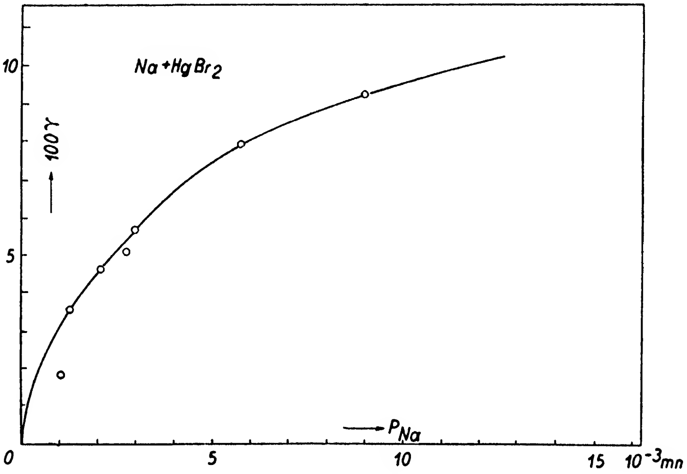


Fig. 21.—Dependence of the light yield γ on the partial pressure of the Na-vapour for $Na + HgBr_2$.

In contradistinction to the Cl_2-flame we do not have a free atom formed in the primary reaction, but instead, the diatomic radical HgCl. As the latter reacts with the atomic Na-vapour according to the double decomposition assumed for the secondary reaction, there is no reason why Na_2-molecules should be specially preferred, and they will in fact only react proportionately to their very small concentration and thus play no appreciable part. All the phenomena which in the case of the halogen flames we attributed to the Na_2-molecules should consequently be absent here, and this is indeed found to be the case. In the first place the heating of the reaction zone has no extinguishing effect; secondly, the curve of the light yield has an entirely different shape from that for the halogen flames. The reason for this is that the increase of the light yield is now due to the fact that the number of NaCl-molecules reaching the wall without colliding with sodium atoms decreases as the pressure increases. This gives rise to a convex curve as shown in Fig. 21.

Here, too, the reaction velocity constants for all the primary and secondary reactions are of the order of magnitude for reactions which are successful at every collision. The same order of magnitude is still retained if K-vapour is substituted for Na-vapour.

Likewise, the last group of reactions to be subject to detailed examination, i.e. the reactions of sodium and potassium vapour with the hydrogen halides, were also found by SCHAY[6] to be almost entirely lacking in inertia. In these cases, it has up till now been possible to determine the primary reaction only. For sodium vapour and hydrogen chloride, for instance, the primary reaction is

$$\mathrm{Na} + \mathrm{ClH} \rightarrow \mathrm{NaCl} + \mathrm{H}$$

and follows an analogous scheme in all the other cases. The fate of the H-atoms split off in the primary reaction and the way in which their reactions effect the excitation of light have not yet been elucidated. As shown in Table II, some of the six primary reactions are slightly endothermic. Even though these have no genuine reaction inertia, they are subject to a yield factor $e^{-Q/RT}$ which contains the heat of reaction in the exponent. The Table compares the velocity constants which have been calculated by taking this coefficient into account with the ones

TABLE II

Reaction	Heat of Reaction in kg.-cal	$k_{\text{exp.}}$ at 600°	$k_{\text{theor.}}$ at 600°	$\frac{k_{\text{exp.}}}{k_{\text{theor.}}}$
Na + HCl	− 5·1	$1 \cdot 10^{-9}$	$1 \cdot 10^{-7}$	0·01
Na + HBr	− 1·6	$2{\cdot}5 \cdot 10^{-8}$	$9 \cdot 10^{-8}$	0·3
Na + HJ	0	$2 \cdot 10^{-7}$	$8 \cdot 10^{-8}$	2·5
K + HCl	− 2·2	$4 \cdot 10^{-8}$	$8 \cdot 10^{-8}$	0·5
K + HBr	+ 1·6	$1{\cdot}5 \cdot 10^{-7}$	$7 \cdot 10^{-8}$	2·0
K + HJ	+ 5·0	$8 \cdot 10^{-7}$	$7 \cdot 10^{-8}$	11·5

experimentally determined; and it shows once more that the actual speed is never smaller, but rather is often appreciably greater than the calculated limiting velocity.

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For a detailed review of the work discussed in this Section, see G. Schay, Fortschr. d. Chemie, Physik und physikalischen Chemie, 21 (1930).

SECTION THREE

ON ATOMIC REACTIONS POSSESSING ENERGY OF ACTIVATION

At the opening of the preceding Section it was explained that we must expect very simple laws to apply to atomic reactions. The account that was given of numerous atomic reactions, the velocities of which had been measured by the method of highly dilute flames, has strongly confirmed this expectation. The simplicity of the laws seemed to go even farther than is really desirable from the point of view of our ultimate aim. For if all atomic reactions are successful at every collision it means that chemical differences are playing no part at all, so that it would appear hopeless to attempt to extract from our results any information as to the delicately graded differences between ordinary reactions.

Fortunately, however, certain other atomic reactions are not so completely lacking in reaction inertia, and hence are not so stereotyped in their course, as those discussed up till now. One important example of an atomic reaction possessing a heat of activation, viz. the parahydrogen transformation, we have already encountered in the first Section. But in addition to this there exists a large group of atomic reactions, covering an exceedingly wide field, preliminary results for which it is now proposed to discuss. The reactions in question are those of Na-vapour with the organic halogen compounds, as, for instance,

$$\mathrm{Na} + \mathrm{ClCH_3} \rightarrow \mathrm{NaCl} + \mathrm{CH_3}$$

or, in generalized form,

$$\mathrm{Na} + \mathrm{HlR} \rightarrow \mathrm{NaHl} + \mathrm{R}$$

The field of experimental investigation thus opened up is very extensive owing to the fact that we have at our disposal not only the four halogens, but also a very wide range of organic radicals which will combine with them. Consequently the work done up to the present has been restricted to the examination of the simplest cases, so that the picture we shall be able to draw is but a preliminary sketch. It is hoped, however, that it will soon be considerably amplified.

The method of highly dilute flames is in most cases not suitable for the measurement of the velocity of these reactions, and accordingly a new method has had to be devised. One reason for this is that the use of highly dilute flames at once becomes difficult unless the reaction is successful at every collision or so, for the length of the tube necessary becomes inordinately great. A further obstacle is that the reactions of sodium vapour with organic halogen compounds are not accompanied by luminescence, so that it is very difficult to judge to what extent the reaction takes place on the wall.

We have therefore devised in collaboration with v. HARTEL[1] a new method, in which these difficulties are avoided. This method includes the principles of the highly dilute flames in so far as once again the rate of reaction is determined by measuring the distance which one component can penetrate into the other before it is consumed by the reaction. However, in order to measure slow reactions, this distance is shortened by increasing the diffusion resistance by the addition of a foreign gas. In addition the apparatus is so disposed that the occurrence of a wall reaction is eliminated.

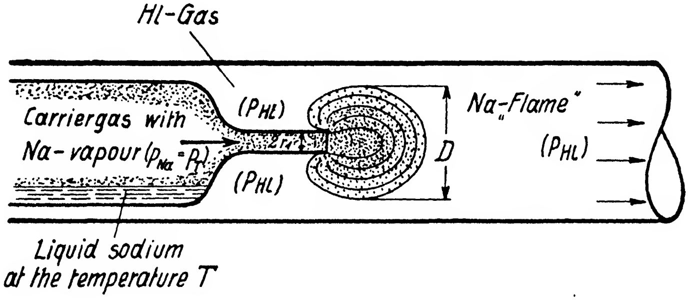


FIG. 22.—Arrangement for the measurement of slow reactions of Na-vapour (diffusion method).

Some idea of the experimental arrangement and of the method of working is given by the diagram in Fig. 22. The apparatus contains an excess of the foreign gas already mentioned, which serves not only to increase the diffusion resistance, but also to regulate the flow. As such foreign gas—or "carrier gas," as we shall call it—we generally use H_2 or N_2 at a pressure of 2–10 mm. The carrier gas first flows through a container holding liquid sodium at about 250° C. (as shown in the figure), and thus becomes charged with Na-vapour up to a partial pressure of about 2×10^{-3} mm. The gas stream conveys the Na-vapour into the reaction space where it reacts with the halogen which is present there under a partial pressure of something between a few hundredths and a few tenths of a millimetre. By exciting the fluorescence of the sodium vapour by means of a resonance lamp it is possible to see how far the sodium vapour can diffuse into the halogen gas before its concentration has reached the limit of detectability. From the diameter of the "sodium flame" which results, the reaction velocity can be calculated if the partial pressure of the halogen compound is known.

It is evident that here, as in the case of highly dilute flames, the extent of the region of mutual interpenetration of the components—i.e. in this instance the "sodium flame"—increases as the velocity of the reaction decreases; and it is to be expected that this inverse relation should likewise be capable of definite formulation in a mathematical equation.

One assumption that may be made is that the flow of the inert gas shall be fast enough to convey the Na-vapour into the reaction tube without its concentration being previously impaired to any appreciable extent by reaction with the halogen compound which, of course, will always diffuse to a certain degree into the jet against the stream of carrier gas. According to this assumption the Na-vapour would flow through the jet into the reaction tube with the same partial pressure p_T with which it was originally taken up by the inert gas.

The second starting-point of the calculation is the assumption already tacitly introduced above, i.e. that the rate of flow of carrier gas in the reaction tube would (unlike that inside the jet) be so slow that the distribution of the reacting components would be effected exclusively by way of diffusion, the influence of the flow being negligible. In particular the distribution of the halogen compound in the carrier gas should be uninfluenced by the flow of the latter, so that, ignoring for the moment its consumption by the Na-vapour, the halogen compound should have the same partial pressure (p_{HI}) throughout the entire reaction space. It would thus be immaterial where the halogen compound entered this space; and for this reason the point of entry has been only roughly indicated in the figure.

As the halogen compound is always employed in considerable excess compared with the Na-vapour, its consumption by the reaction can in fact be disregarded. Thus the only question remaining is whether it is possible in practice to regulate the flow of the carrier gas in the manner described so that in the stationary state the partial pressure of the halogen compound remains constant at p_{HI} all over the reaction space, and yet suddenly sinks to zero just at the orifice of the jet.

The attainment of these conditions has been checked by direct measurement of the partial pressure of the halogen compound at various distances from the jet during the flow of the carrier gas. In this way certain limits of flow and pressure of the carrier gas were found within which the desired conditions were realized to a sufficient degree of accuracy.

As in the case of highly dilute flames, it must once more be postulated as a condition for the stationary state, that in every space element of the reaction zone the rate of consumption of any given reactant must be exactly equal to its rate of accumulation by diffusion. Since, as just demonstrated, the partial pressure of the halogen compound is constant throughout at p_{HI} mm., we only need to take into consideration the differential equation relating to the sodium pressure. This can be written, assuming a spherical expansion from the jet mouth, as

$$-\,kp_{\mathrm{HI}}\cdot p_{\mathrm{Na}}+\delta\left(\frac{d^2p_{\mathrm{Na}}}{dr^2}+\frac{2}{r}\,\frac{dp_{\mathrm{Na}}}{dr}\right)=0\quad.\quad.\quad.\quad.\quad(6)$$

where r is the radius of the jet.

The first term represents the loss of sodium vapour taking place in the space element under examination (spherical shell) as a result of the reaction. The second and third terms represent the compensation of this loss through diffusion.

This equation must now be integrated between the limits $p_{\mathrm{Na}}=p_{\mathrm{T}}$ which holds at the mouth of the jet, and the pressure at the boundary of the "Na-flame" made visible by the resonance light. The boundary line of this flame is determined by the decrease of p_{Na} below the limit of detectability, i.e. below the point at which the partial pressure p_{Na} is just sufficient to cause the emission of an observable resonance light. If this limiting pressure obtaining at the edge of the "flame" be p_0, the diameter of the flame D, and the radius of the jet r_1, we arrive at the integrated equation

$$\frac{p_{\mathrm{T}}}{p_0}=\frac{\mathrm{D}}{2r_1}e^{-\sqrt{\frac{kp_{\mathrm{HI}}}{\delta}}}\left(p-\frac{\mathrm{D}}{2}\right)\quad.\quad.\quad.\quad.\quad.\quad(7)$$

This equation permits us to determine the velocity constant k, if the diffusion constant δ is known. By varying the partial pressure p_{HI} the diameter D of the flame may be adjusted to different values and thus a series of different estimates of k is obtained.

Actually, in our calculations, a simpler form of equation, obtained by disregarding the spherical expansion in the above differential equation, was used. This assumption leads to the elimination of the last term of equation (6), and we thus have

$$-k \cdot p_{\mathrm{HI}} \cdot p_{\mathrm{Na}} + \delta \frac{d^2 p_{\mathrm{Na}}}{dr^2} = 0 \quad . \; . \; . \; . \; . \; . \quad (8)$$

which, on integration, gives

$$p_{\mathrm{Na}} = p_{\mathrm{T}} \cdot e^{-\sqrt{\frac{k p_{\mathrm{HI}}}{\delta}} \cdot r}$$

and

$$k = \frac{\left(\log_e \frac{p_{\mathrm{T}}}{p_0}\right)^2}{\frac{\mathrm{D}^2}{4}} \cdot \frac{\delta}{p_{\mathrm{HI}}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

This formula shows, as we expected, that the calculated velocity constant varies inversely as the experimentally observed diameter of the flame, or, more exactly, is inversely proportional to the square of this diameter. The formula further makes it clear that when the reactant is varied—i.e. when different halogen compounds are used—the different partial pressures which must be employed in order to get the same flame diameter must be inversely proportional to the velocity constants of the reacting substances.

The wide range covered by the reaction rates of the different halogen compounds can best be seen by observing the range of partial pressures which have to be employed in, say, the case of the four methyl halides (methyl iodide, bromide, chloride, fluoride) in order to bring the sodium flame up to a certain magnitude. At one end of the homologous series, i.e. at methyl iodide, pressures of the order 1/1,000th mm. are sufficient, whereas at the other end, i.e. for methyl fluoride, it is found that even with a pressure of 10 mm. of the gas, the tube is still entirely filled with Na-vapour. This means that the rate of reaction for methyl iodide corresponds roughly to success at every collision, whilst the behaviour of methyl fluoride indicates that less than one in a million collisions with Na-atoms is successful. The two intermediate homologues, methyl bromide and methyl chloride, stand between these two extremes; the former reacts at every fifty collisions or so and the latter at every ten thousand.

It is clear therefore that the range covered by the reaction velocities is very wide indeed; in fact, as already indicated, it is so great as to overstep the limits of practical applicability of the method. Thus it has, up to the present, not been possible to use the very high pressures of halogen compound which would be required, say, in the measurement of the reaction between Na and methyl fluoride; that is, we are, as yet, unable to measure reactions which go more slowly than at every hundred thousand collisions. On the other hand, the method is fundamentally unsuitable for reactions occurring at a greater speed than at every tenth collision or so, for in these cases it becomes impossible to realize the condition that the halogen compound shall be in excess of the Na-vapour in the interior of the Na-flame. At the moment, therefore, our studies must be limited to reactions which are successful once in every ten to hundred thousand collisions.

Accordingly, it is within this range that the results about to be described have been obtained.[2] Our aim being to discover some connection with ordinary chemical reactions I shall particularly stress the gradation of reaction velocities (which is expressed in the number of collisions needed for one successful transformation). The data are preliminary ones and their reliability is impaired in particular by the fact that the values of the diffusion constant of the Na-vapour, which are indispensable to the calculation of the velocity constant according to equation (9), have not as yet been determined with sufficient accuracy. The figures to be quoted should therefore be regarded as strictly preliminary in nature, and it is hoped that in due course they will be improved upon.

The first gradation which is found when the halogens are varied in the order fluorine, chlorine, bromine, iodine, has already been mentioned. We have satisfied ourselves that this regularity also exists in other cases: thus it has been found in the series ethyl chloride, ethyl bromide, ethyl iodide, and also in the series phenyl chloride, phenyl bromide, phenyl iodide. (Compare Series 1.)

SERIES 1

INCREASE OF THE REACTION VELOCITY IN THE SERIES FLUORINE, CHLORINE, BROMINE, IODINE

	$> 10^6$	10,000	50	1
1.	$CH_3F \rightarrow$	$CH_3Cl \rightarrow$	$CH_3Br \rightarrow$	CH_3I
2.		$C_2H_5Cl \rightarrow$	$C_2H_5Br \rightarrow$	C_2H_5I
3.		$C_6H_5Cl \rightarrow$	$C_6H_5Br \rightarrow$	C_6H_5I

(Differences in the second and third lines nearly the same as in the first.)

From the results it will be seen that the chlorine compounds are of particular value in this work, in that they are the most suitable subjects for an investigation of the influence of the different organic radicals on reactivity. The bromine compounds and even more so those of iodine react too rapidly for any distinct gradation to be apparent; on the other hand the reactions with fluorine compounds are so slow that their velocities can scarcely be measured at all. For this reason the following investigations into the gradation of reactivity have all been carried out with chlorine compounds. The results are included in the following Series 2–7 (see pages 56–59). These show us that an increase in the rate of reaction is produced by the following factors:

(1) Lengthening of the carbon chain (Series 2).

(2) Passage from primary to secondary to tertiary carbon (Series 4).

(3) Carbon double bond in the neighbouring position (Series 6).

(4) Oxygen atoms (Series 6).

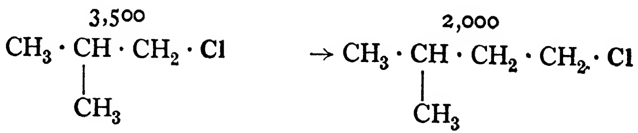
(5) Multiple substitution. The more Cl-atoms that are present and the closer they are together the greater is the effect. A retardation of the reaction rate results if the Cl-atom is attached to the double-bonded C-atom (Series 5).

SERIES 2

INCREASE OF THE REACTION VELOCITY WITH INCREASING LENGTH OF THE CARBON CHAIN

1. $\overset{10{,}000}{\mathrm{CH_3\cdot Cl}} \rightarrow \overset{7{,}000}{\mathrm{CH_3\cdot CH_2\cdot Cl}} \rightarrow \overset{4{,}400}{\mathrm{CH_3\cdot CH_2\cdot CH_2\cdot Cl}} \rightarrow \overset{3{,}300}{\mathrm{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot Cl}} \rightarrow \overset{2{,}200}{\mathrm{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot Cl}}$

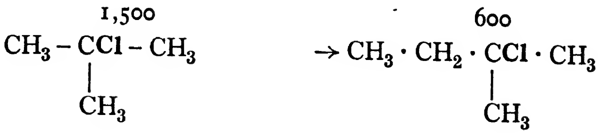
2.



$\overset{3{,}500}{\mathrm{CH_3\cdot \underset{\substack{|\\ CH_3}}{CH}\cdot CH_2\cdot Cl}} \rightarrow \overset{2{,}000}{\mathrm{CH_3\cdot \underset{\substack{|\\ CH_3}}{CH}\cdot CH_2\cdot CH_2\cdot Cl}}$

3. $\overset{3{,}300}{\mathrm{CH_3\cdot CH\cdot Cl\cdot CH_3}} \rightarrow \overset{2{,}200}{\mathrm{CH_3\cdot CH_2\cdot CH\cdot Cl\cdot CH_3}}$

4.



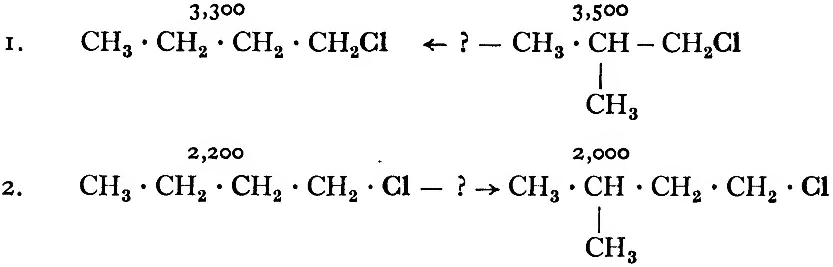
$\overset{1{,}500}{\mathrm{CH_3-\underset{\substack{|\\ CH_3}}{CCl}-CH_3}} \rightarrow \overset{600}{\mathrm{CH_3\cdot CH_2\cdot \underset{\substack{|\\ CH_3}}{CCl}\cdot CH_3}}$

5. $\overset{900}{\mathrm{CH_2\cdot Cl_2}} \rightarrow \overset{650}{\mathrm{CH_3\cdot CH\cdot Cl_2}} \rightarrow \overset{300}{\mathrm{CH_3\cdot CH_2\cdot CH\cdot Cl_2}}$

A branching of the chains, which leaves the position of the Cl-atoms undisturbed, has no distinct influence (Series 3).

SERIES 3

BRANCHING OF THE CARBON CHAIN



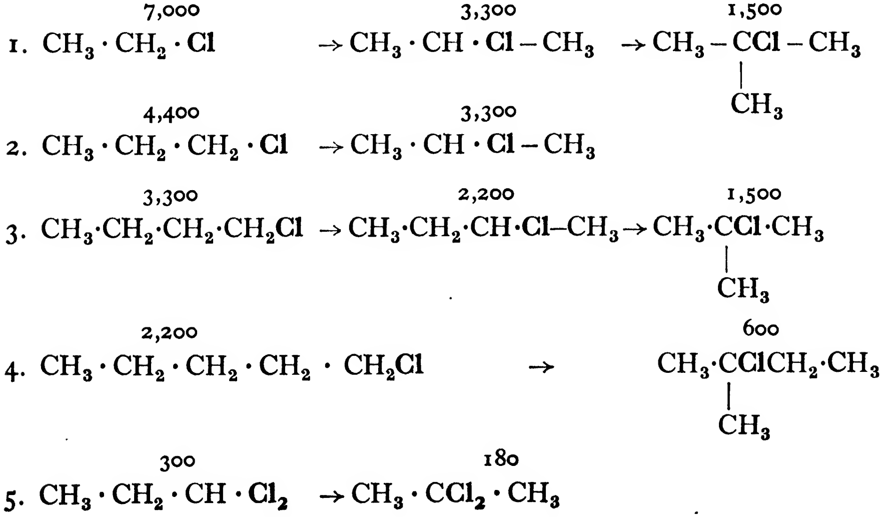
1. $\overset{3,300}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl} \leftarrow ? - \overset{3,500}{CH_3 \cdot \underset{\underset{\textstyle CH_3}{|}}{CH} - CH_2Cl}$

2. $\overset{2,200}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot Cl} - ? \rightarrow \overset{2,000}{CH_3 \cdot \underset{\underset{\textstyle CH_3}{|}}{CH} \cdot CH_2 \cdot CH_2 \cdot Cl}$

On the strength of these preliminary results we may venture to say that of the expectations with which we began the study of atomic reactions, one at any rate certainly seems to have been realized, viz. that the laws prevailing in this field are very explicit and simple. We must now ask what are the chances of extending these rules so as to apply, not only to atomic reactions, but also to ordinary chemical reactions.

SERIES 4

INCREASE OF THE REACTION VELOCITY IN THE ORDER: PRIMARY, SECONDARY, TERTIARY



1. $\overset{7,000}{CH_3 \cdot CH_2 \cdot Cl} \rightarrow \overset{3,300}{CH_3 \cdot CH \cdot Cl - CH_3} \rightarrow \overset{1,500}{CH_3 - \underset{\underset{\textstyle CH_3}{|}}{CCl} - CH_3}$

2. $\overset{4,400}{CH_3 \cdot CH_2 \cdot CH_2 \cdot Cl} \rightarrow \overset{3,300}{CH_3 \cdot CH \cdot Cl - CH_3}$

3. $\overset{3,300}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl} \rightarrow \overset{2,200}{CH_3 \cdot CH_2 \cdot CH \cdot Cl - CH_3} \rightarrow \overset{1,500}{CH_3 \cdot \underset{\underset{\textstyle CH_3}{|}}{CCl} \cdot CH_3}$

4. $\overset{2,200}{CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl} \rightarrow \overset{600}{CH_3 \cdot \underset{\underset{\textstyle CH_3}{|}}{CCl} CH_2 \cdot CH_3}$

5. $\overset{300}{CH_3 \cdot CH_2 \cdot CH \cdot Cl_2} \rightarrow \overset{180}{CH_3 \cdot CCl_2 \cdot CH_3}$

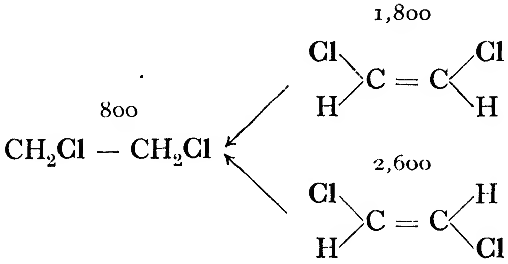
SERIES 5

INHIBITION OF THE REACTION WITH THE CHLORINE ATOM ATTACHED TO A DOUBLY BOUND C-ATOM

1. $\overset{7,000}{CH_3 \cdot CH_2Cl} \leftarrow \overset{11,000}{CH_2 = CHCl}$

2. $\overset{3,300}{CH_3 \cdot CH \cdot ClCH_3} \leftarrow \overset{5,500}{CH_2 = C \cdot Cl - CH_3}$

3.


1,800
Cl
Cl
C = C
H
H
800
CH2Cl — CH2Cl
2,600
Cl
H
C = C
H
Cl

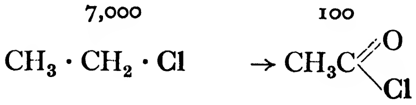
SERIES 6

INCREASE OF THE REACTION VELOCITY CAUSED
(*a*) BY THE PROXIMITY OF A DOUBLY BOUND
(*b*) BY OXYGEN

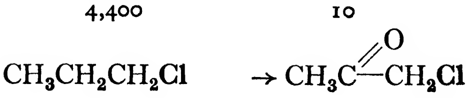
(*a*) 1. $\overset{4,400}{CH_3 \cdot CH_2 \cdot CH_2Cl} \rightarrow \overset{250}{CH_2 = CH - CH_2Cl}$

(2. $\overset{10,000}{CH_3Cl} \rightarrow \overset{1}{C_6H_5 \cdot CH_2 \cdot Cl}$)

(*b*) 3.


7,000
CH3 · CH2 · Cl
100
CH3C
O
Cl

4.


4,400
CH3CH2CH2Cl
10
O
CH3C—CH2Cl

SERIES 7

INCREASE OF THE REACTION VELOCITY WITH INCREASING NUMBER OF CHLORINE ATOMS. GREATER EFFECT WITH SMALLER SEPARATIONS

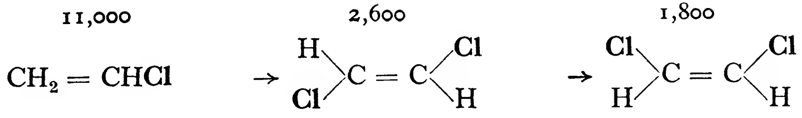
1. $\overset{10{,}000}{CH_3 \cdot Cl} \rightarrow \overset{900}{CH_2 \cdot Cl_2} \rightarrow \overset{100}{CH \cdot Cl_3} \rightarrow \overset{25}{C \cdot Cl_4}$

2. $\overset{7{,}000}{CH_3 \cdot CH_2Cl} \rightarrow \overset{800}{CH_2 \cdot Cl \cdot CH_2Cl} \rightarrow \overset{650}{CH_3 \cdot CH \cdot Cl_2}$

3. $\overset{4{,}400}{CH_3 \cdot CH_2 \cdot CH_2Cl} \rightarrow \overset{1{,}000}{CH_2Cl \cdot CH_2 \cdot CH_2Cl} \rightarrow \overset{500}{CH_3 \cdot CH \cdot Cl \cdot CH_2Cl} \rightarrow \overset{300}{CH_3 \cdot CH_2 \cdot CHCl_2}$

4. $\overset{3{,}300}{CH_3 \cdot CH \cdot Cl \cdot CH_3} \rightarrow \overset{180}{CH_3 \cdot C \cdot Cl_2 \cdot CH_3}$

5.



6. $\overset{900}{\rightarrow CH_2Cl_2} \rightarrow \overset{800}{CH_2Cl - CH_2Cl} \leftarrow \overset{1{,}000}{CH_2Cl - CH_2 - CH_2Cl}$

(In the sixth line there are two effects in opposition: the lengthening of the C-chain increasing the reaction velocity and the simultaneous separation of the Cl-atoms reducing it.)

This question has up till the present only been attacked with the aid of the material available in the literature.[3] The difficulty encountered here is that we meet a great many reactions, widely different in nature, for none of which the mechanism is known. It was therefore necessary to select certain reactions for which it would be justifiable to assume some mechanism analogous to the simple scheme

$$\mathrm{Na} + \mathrm{HlR} \rightarrow \mathrm{NaHl} + \mathrm{R}$$

of atomic reactions. This appeared to us to be the case for certain reactions in which a single ion reacts with a single molecule. Several such reactions are known involving negative ions ("negative mechanism"), such as

$$\mathrm{I^-} + \mathrm{CH_3Cl} \rightarrow \mathrm{ICH_3} + \mathrm{Cl^-}$$

$$\mathrm{S_2O_3^{--}} + \mathrm{CH_3Cl} \rightarrow \mathrm{{}^-S_2O_3\ CH_3} + \mathrm{Cl^-}$$

But in addition positive ions, especially the H^+-ion, would also seem to be capable of such action ("positive mechanism") as in the case of the saponification of ethers by acids, which accordingly should be written in the form

$$\mathrm{H^+} + \mathrm{R_1{-}O{-}R_2} \rightarrow \mathrm{R_1OH} + \mathrm{R_2^+}$$

followed by

$$\mathrm{R_2^+} + \mathrm{Cl^-} \rightarrow \mathrm{R_2Cl}$$

These two ionic mechanisms seemed similar enough to our gas reactions with Na-vapour to tempt us to search for some parallelism between the rates of reaction of the two groups. A study of all the experimental material available in the literature has led to the results shown roughly in Table III (page 61).

A comparison of the ionic reactions with the corresponding reactions of the Na-vapour reveals a parallelism in that the rate of reaction is again increased in the order F, Cl, Br, I, and further that a double bond in the neighbouring position, or a carbonyl group, likewise produces an increase. If we set aside a few cases which seem to be somewhat uncertain, this parallelism is equally pronounced in the increase of the rate of reaction brought about by multiple substitution. The retarding influence which a double bond exercises over the substituent attached to the doubly bound carbon atom is also identical. On the other hand it must be noted that the prolongation of the carbon chain mostly exerts a strong retarding influence, particularly in the case of transition from methyl to ethyl, whereas gas reactions with Na-vapour show a gradation in the opposite sense.

The accord in the gradation of reaction rates, between the reactions involving Na-vapour and those involving ions, is thus very far-reaching, though not absolutely complete. A discrepancy which may be cleared up in an interesting fashion is revealed by a comparison of the gradation in the series primary to secondary to tertiary. In the reactions with Na-vapour there is an increase in velocity as we pass along the series. This is true, however, only of a few of the ionic reactions—those in which the $H^{\bullet}$-ion participates—and the reactions produced by negative ions show an opposite order of velocities, usually described as "steric hindrance."

TABLE III

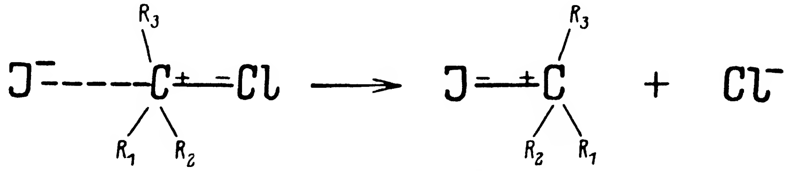
Reaction Velocity and Structure

Gas Reactions in Sodium Vapour and Ionic Reactions in Solution

	Reaction with Na-Vapour	Ionic Reaction	
		Negative Mechanism	Positive Mechanism
Series F, Cl, Br, I	Increase	Increase	
C = C in neighbouring position	Increase	Increase	
C = O	Increase	Increase	
Multiple substitution	Increase	Increase	
C = CCl in place of C − CCl	Decrease	Decrease	
Lengthening of the chain	Decrease	Increase	
Branching of the chain	No effect	Decrease	
Primary → secondary → tertiary	Increase	Decrease	Increase

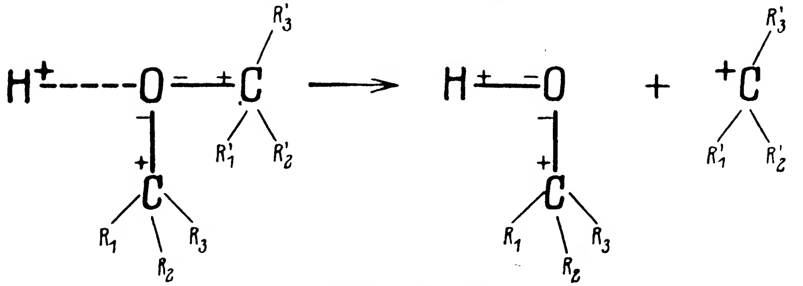
Now it is easy to see that such a steric hindrance cannot occur in connection with a positive ion mechanism, whereas it is to be expected straightway with a negative one; for, if we take into account the fact that the groups with which these ions react are dipoles, it is to be assumed that the action always starts from that end of the dipole having a charge opposite to the charge of the ion. Thus for instance:

IONIC REACTIONS



Negative mechanism

IONIC REACTIONS—*continued*

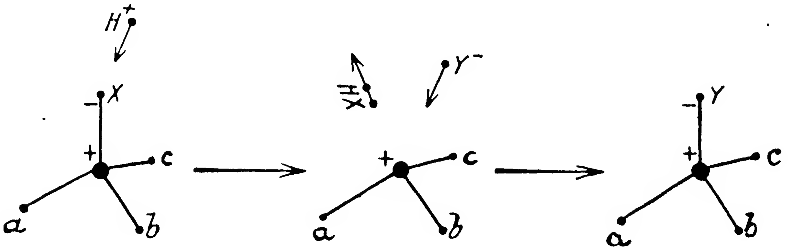


Positive mechanism

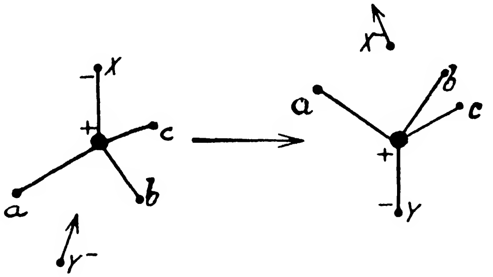
Hence it is to be anticipated that in the case of a negative mechanism the reaction will be hindered by the presence of large substituents attached to the carbon atom, whereas this is impossible in the case of a positive mechanism.

From this conception of the different mechanism of reaction of positive and negative ions, we can infer another very peculiar difference in the spatial position of the substituents introduced in these two ways. This is made clear by the following diagrammatic representation of the positive and negative ion actions:

SPACIAL REPRESENTATION OF THE SUBSTITUTION ACCORDING TO THE NEGATIVE AND POSITIVE MECHANISM



Positive mechanism: no optical inversion



Negative mechanism: optical inversion

We see that no modification of the configuration takes place in the case of the positive mechanism, whereas in the case of the negative mechanism an optical inversion should occur. And in actual fact, a study of the literature of the subject shows that in all cases in which negative mechanism could be assumed, optical inversion results when an optically active compound takes part in the reaction.

The well-known racemizing effect of the halogen ions on optically active compounds of the same halogen can also be regarded as a confirmation of this view, for the halogen ions would cause an atomic exchange reaction

$$\mathrm{Hl}^- + \mathrm{RHl} \rightarrow \mathrm{HlR} + \mathrm{Hl}^-$$

which, being a negative mechanism, leads to optical inversion, which would, of course, only proceed to the point of equilibrium between the two optical antipodes.

Of the reactions which we suppose to be based on a positive mechanism, the original configuration is, as predicted above, found to be retained in the saponification of stereoisomeric acetals and ketals. On the other hand, in the esterification of optically active alcohols with HCl an inversion of the sign of rotation takes place in several cases, in contradiction to what we should expect, since this is a case of a positive mechanism. It represents, therefore, a deviation from the theory which will have to be cleared up.

In conclusion we may say that the results achieved in this first attempt at the elucidation of ordinary chemical reactions with the aid of atomic reactions seem sufficiently satisfactory to encourage further work in this direction.

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2. The subsequent measurements on the reactions of sodium vapour with organic chlorine compounds were carried out in collaboration with H. v. Hartel and N. Meer.
3. The subsequent part of the Section is an abstract of a study carried out in collaboration with N. Meer, which appears in the Z. Physikal. Chem. Very extensive references to the relevant literature are also quoted there.

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